The challenge of applying the biorefinery concept to Guayule biomass Including the water-based extraction of polyisoprene

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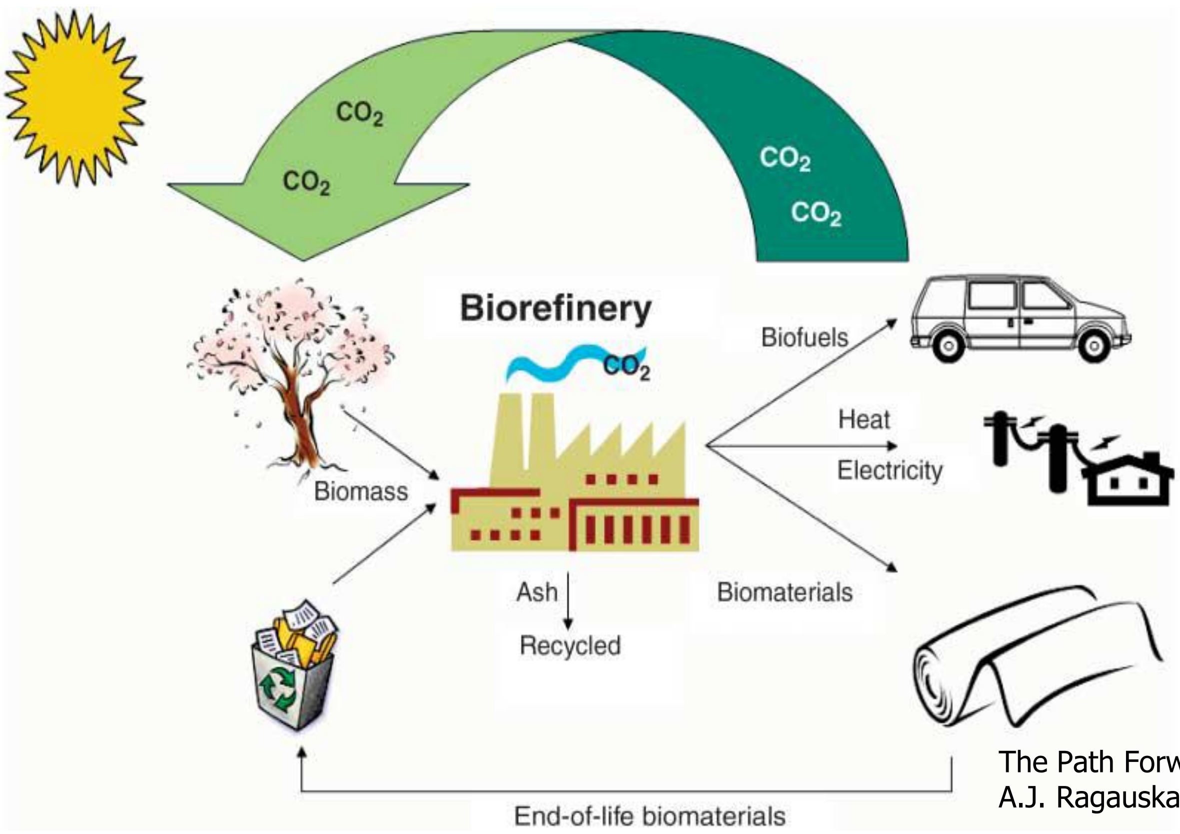
24-25 September 2012, Wageningen

Biorefinery is the sustainable processing of biomass into a spectrum of marketable product s and energy

(Cherunbini 2009; Jungmeier 2009)

The fully integrated agro-biofuel-biomaterial-biopower cycle for sustainable technologies



The Path Forward for Biofuels and Biomaterials, A.J. Ragauskas et al Science 2006

Classification of biorefineries

- Feedstock
  dedicated biomass (Guayule), by-products / starch, oil seeds, forest

- Products
  energy, fibers, polymers, material, additives, bioactive (Guayule)

- Conversion processes
  bio, thermal, chemical, mechanical (Guayule)

Platforms: sugar, oleochemical, lignocellulosic,

One plant may include several platforms (whole biomass)

Many theoretical biorefinery models, often overcrossing

Classification of biorefineries

In short, 2 main cases:

- One biomass → one product (ex. corn to ethanol, or lactic ac.)
  agricultural residues, wood, grasses

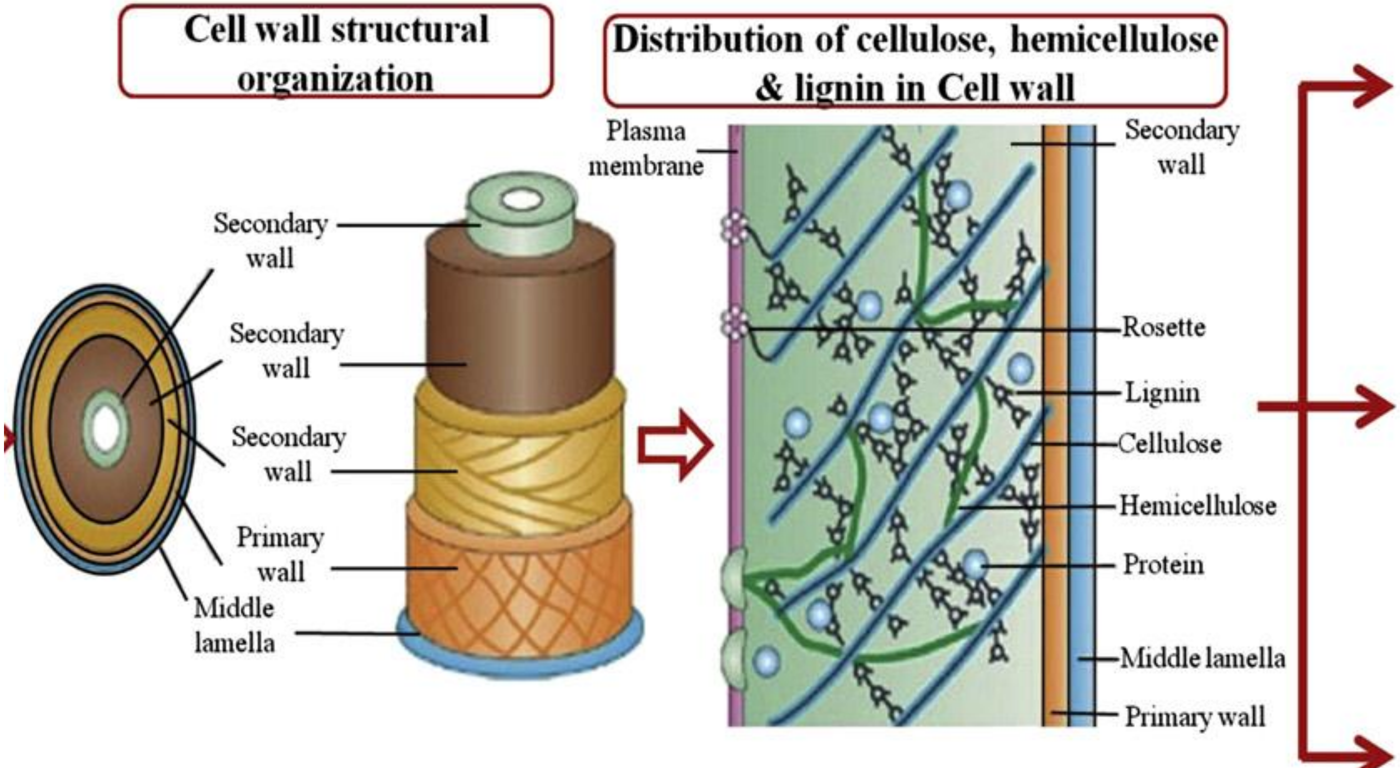
  The most widely developed today

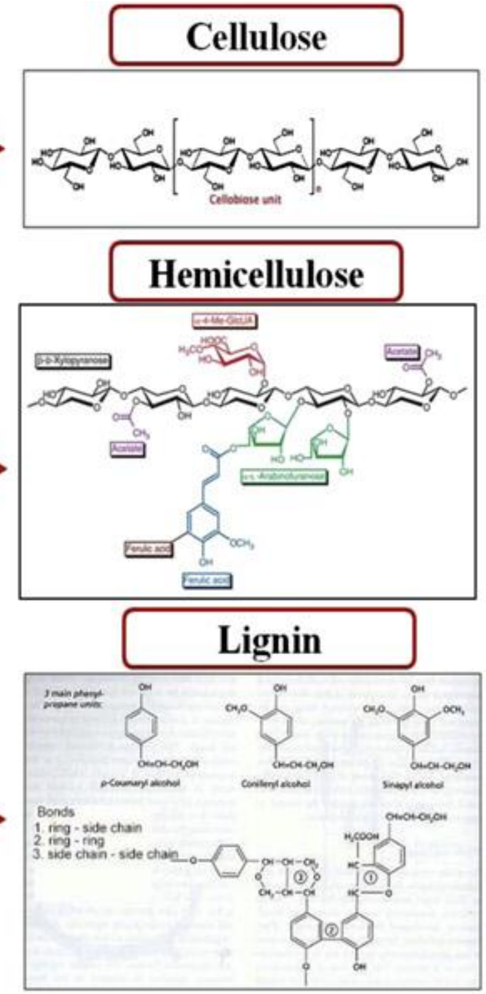
- → multiple prod. biorefinery" a range of products
  (Hulst 1999 ; Sanders 2009)

➡ Biorefining is a complex matter,
even to a single & simple product, like ethanol

Guayule falls within the second case (… even more)

Schematic framework of lignocellulose





Aptitude for bioconversion to ethanol:

Cellulose >> Hemicellulose ; not lignin

➡ **Biorefining is a complex matter, because of biomass complexity**

Menon & Rao 2012

Specific structure of Guayule biomass

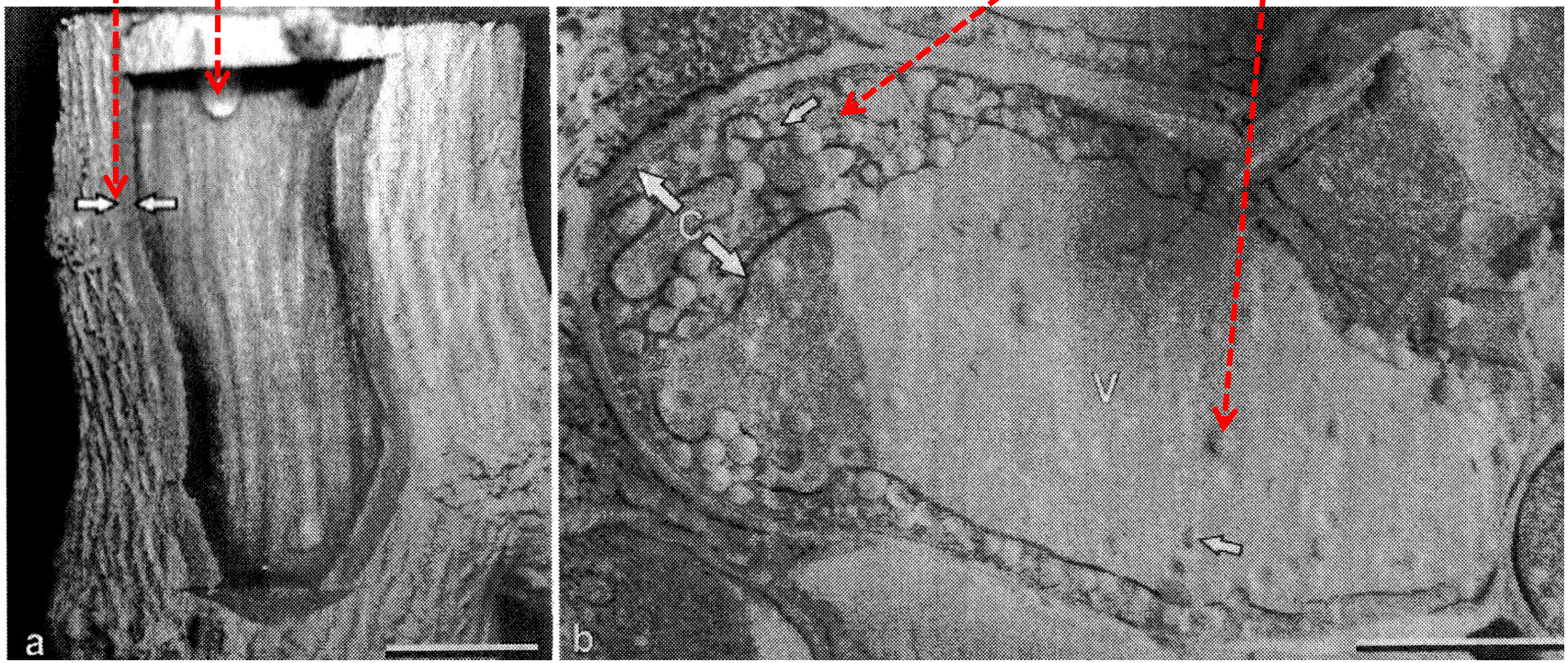
Excised stem segment

CRYO-SEM (young tissue)

Sampled tissue

Resin drop

PI particles in cytosol & vacuoles

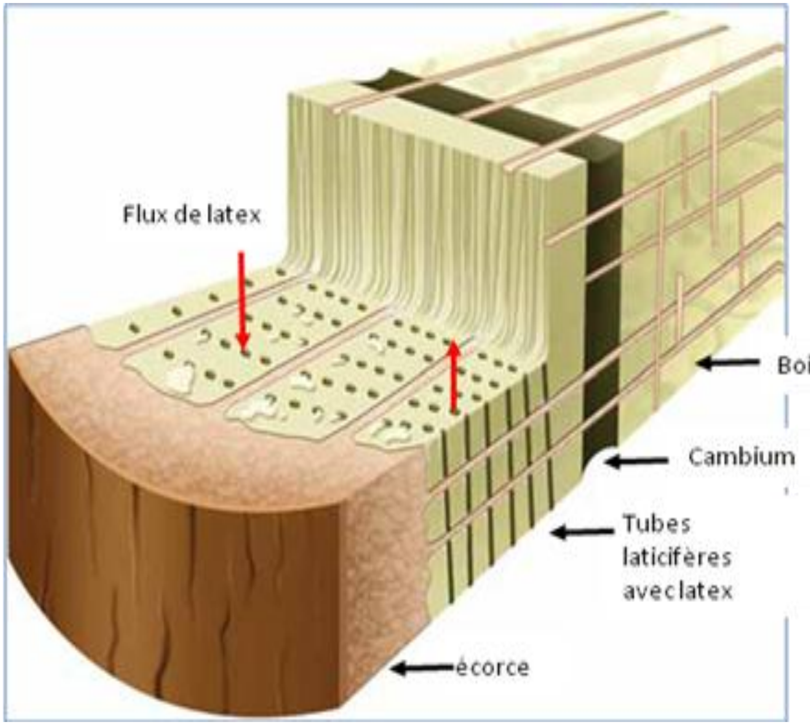


5 mm

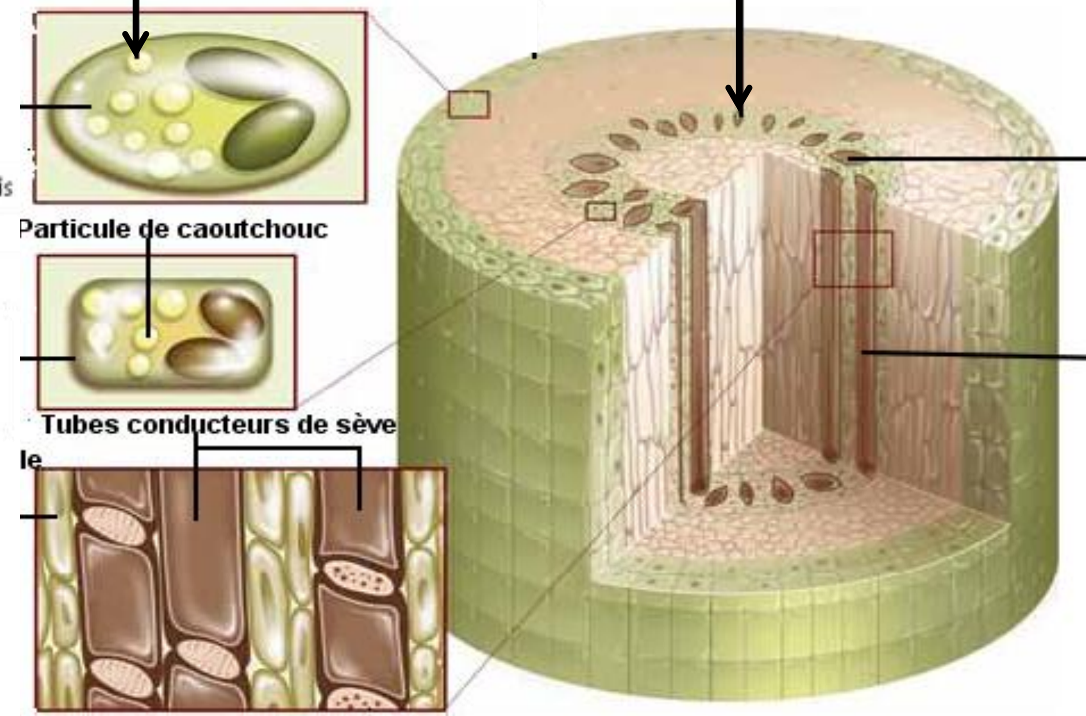
Sce: Cornish & Wood 2002

10 µm

Guayule:
PI entrapped inside cells
resin flows in ducts



Laticifer ducts
in Hevea wood



Sce: Palu & Pioch 2010

➡ **Specific structure of the Guayule biomass**

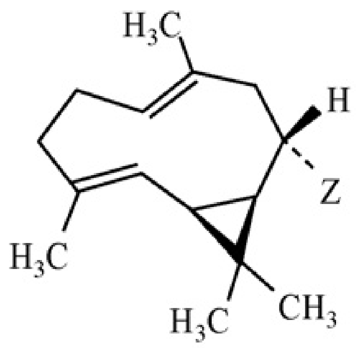
major technical constraint for recovering PI as latex
various localization & types of PI particles
2 low polarity extractable, PI & resin

Chemical composition of guayule extractable

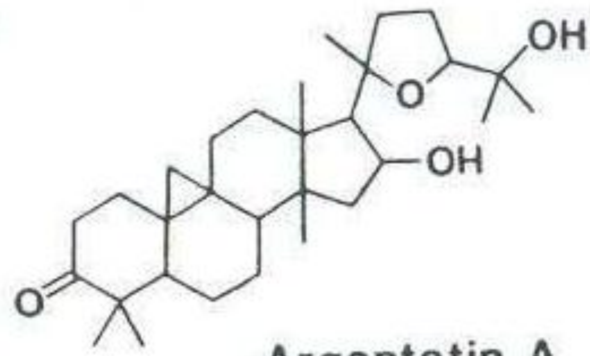
Fraction	Class	Chemicals	Tested uses
Volatile	Terpenes 3-5%	α, β Pinene Camphene, α and β Phellandrene Sabinene, β Myrcene	**Essential oil, Tall oil**
Non-volatile	85-97%		
Water soluble	Short acid, ester Polyphenols	Bornyl acetate, Cinnamic acid Tannins, flavonoides Polysaccharides	**Cockroach attractant**
Water insoluble	Hydrocarbons	α & β Ocimene Limonene	**Termite control** **Nematod control** **Weed control** **Antimicribiol** **Fungistatic** **Adhesives (UF substitutes)** **Strippable coatings** …… New to be discovered
	Fatty acid TG 20-25%	Linoleic (65%), Linolenic, Palmitic , Oleic	
	Wax (leaves)	Carnauba	
	Sesquiterpenes	Guayulines A,B, Partheniol	
	Triterpenes	Argentatine A,B,C,D,E,F,G,H	
	Alkaloid	Guayulamine A,B	

Nakayama 2005, Costa et al 1992, Schloman 1983

Chemical composition of guayule extractible

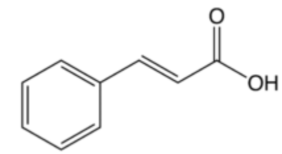


1 Z = *trans*-cinnamate
2 Z = *p*-anisate



Argentatin A

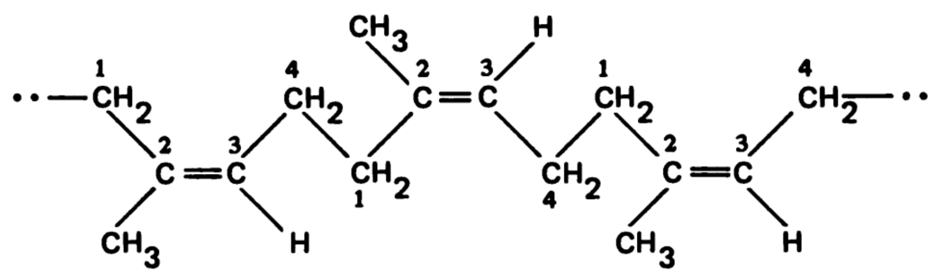
Triterpenoids



Cinnamic acid

Partheniol
Guayulin esters A & B

Sesquiterpenes



cis-1,4-polyisoprene

➡ (Bio) Chemical diversity
brings a challenge for selective extraction

Uses of guayule bagasse (roots, flowers,leaves)

Composite boards

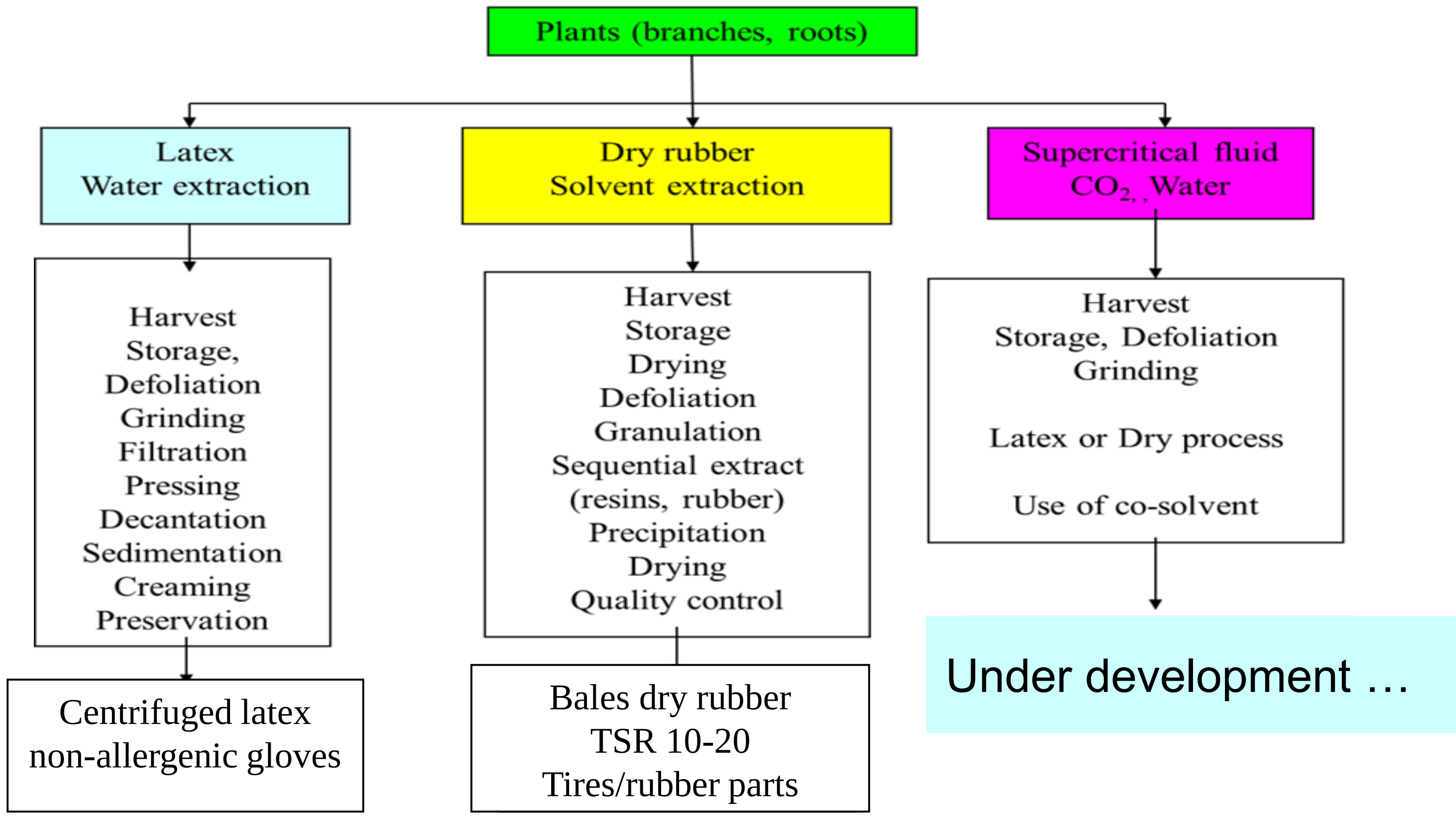
Activated carbon

Soil amendment (deresinated)

Bioenergy / Pellets
Fermentation to ethanol
Thermo-chemical conversion to gas & liquid
-catalytic - to Diesel

➡ An impressive range of products and applications
with positive results
for valorizing the non PI part of harvested biomass (~90%)

3 Types of extraction process for guayule latex & rubber production



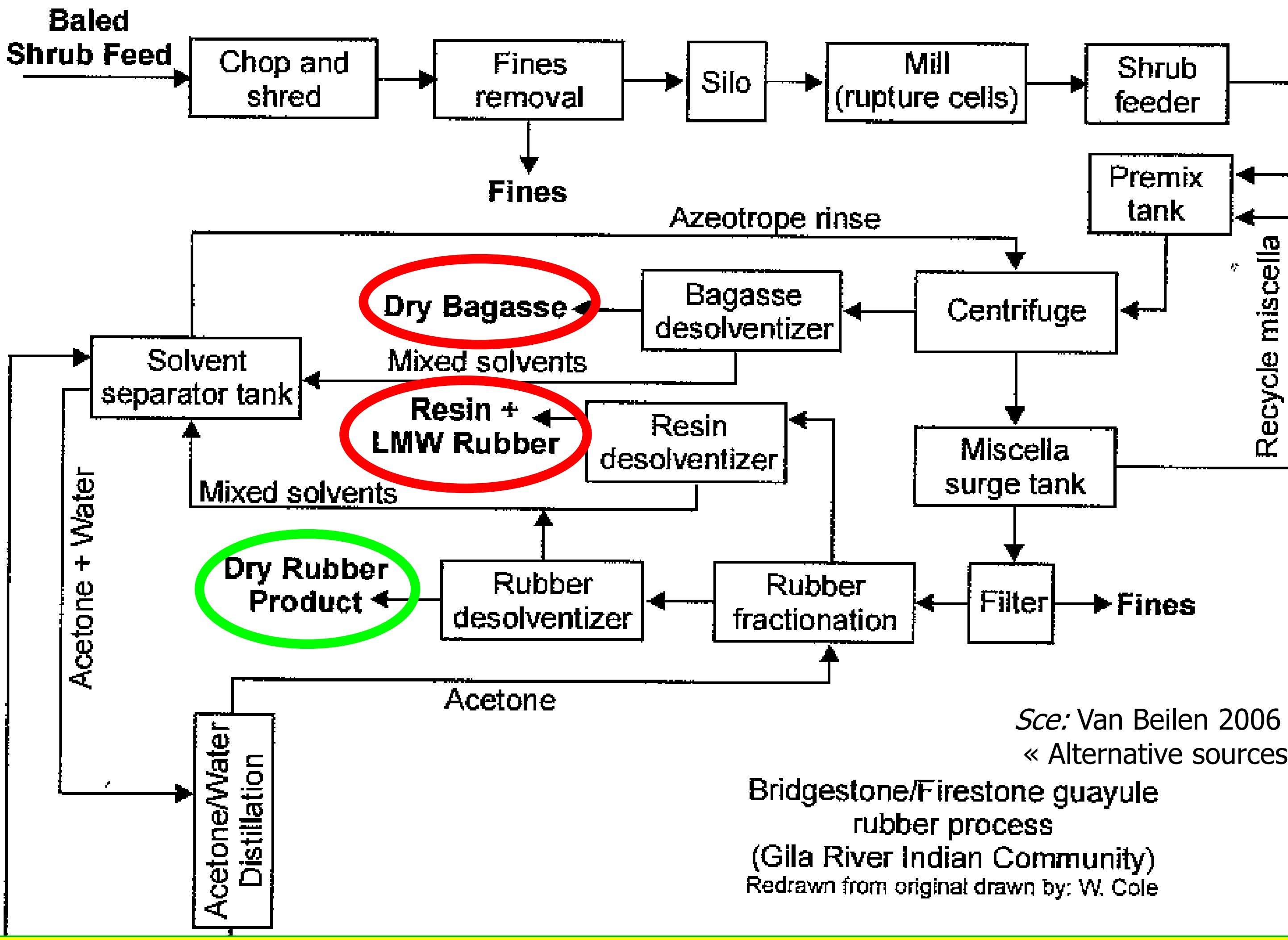
Yulex at USDA station
Casa Grande Az 2004

- CIQA Saltillo Mex.
- Bridgestone/Firestone Sacaton, Az 1980 - 1985
- Texas A&M Univ. 80s

~30 patents since 1949
from Mex. & US groups

Latex & solvent plant of the ERP (Baskerfield, Ca)

Example of “simple” solvent processing facility



Sce: Van Beilen 2006 Epobio report
« Alternative sources of natural rubber »

Bridgestone/Firestone guayule rubber process
(Gila River Indian Community)
Redrawn from original drawn by: W. Cole

➡ Target product was rubber, not resin / (only) a by-product
Process not designed for resin products

Main results /pilot scale latex extraction /EU-Pearls
09/2010 – 07/2012


Cartagena, Spain


Montpellier, France

Harvest

400 kg (dry) biomass harvested, thanks to WUR-PRI & UR 34 Cirad

Biomass analysis

NIRS-based methods for quick determination of PI, MC, resin

taking into account cross contamination of solvent based reference method

(Suchat et al 2012)

“Soft quantitative method for real extraction” of PI avoiding Mw drop

(Bonfils et al, 2012, this conf)

Further chemical analysis of biomass (resin, proteins)

Main results / pilot scale latex extraction 09/2010 – 06/2012

Processing to latex

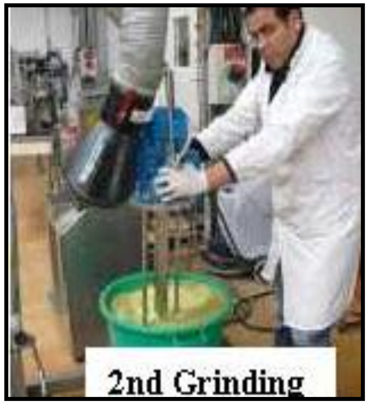
Lab protocol (100g - 1kg) ; assembled – tested a pilot unit (10kg wet)

Pilot scale production: processed 550 kg (Spain) ; 60 kg/day

→ 1.5 kg rubber (tire / Apollo-Vredestein) (Gevers et al. 2012, this conf)

→ 30 L latex (DRC 32%) (CTTM) (Dorget et al 2012, this conf)

Quality control of extracts & products, allergy (Mourton-Gilles et al 2012 this conf)



Rubber & end products from EU-Pearls Guayule

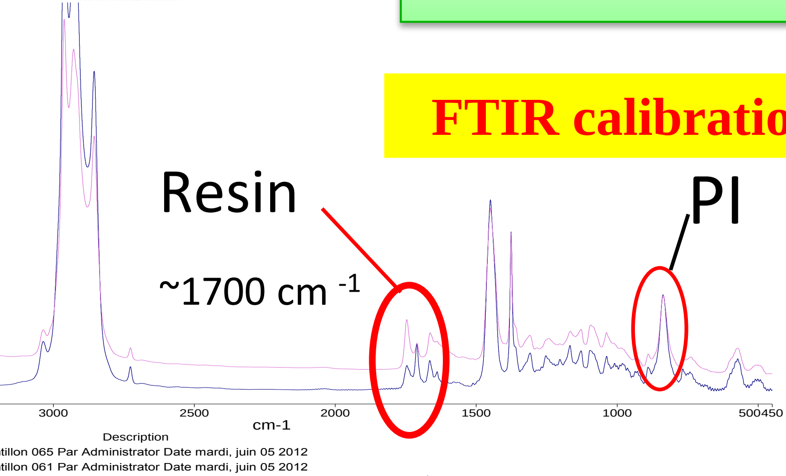
Sce: Cirad 2012
unpublished

Sce: Apollo Vredestein 2012
unpublished

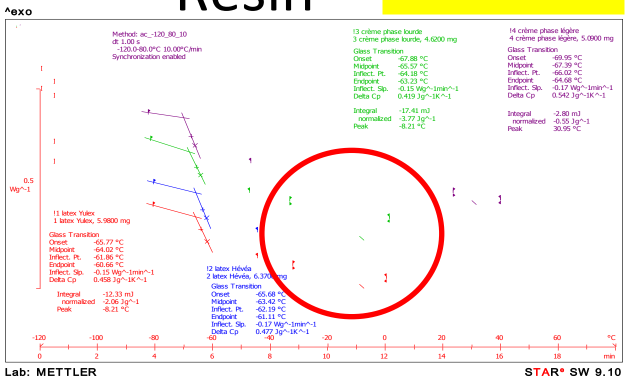
Sce: CTTM Cirad 2012
unpublished

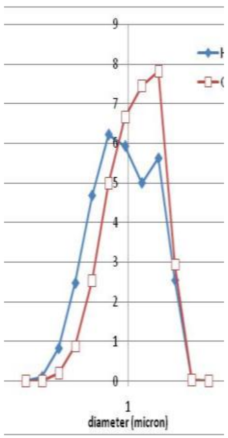
Chemical composition of extracts

FTIR calibration



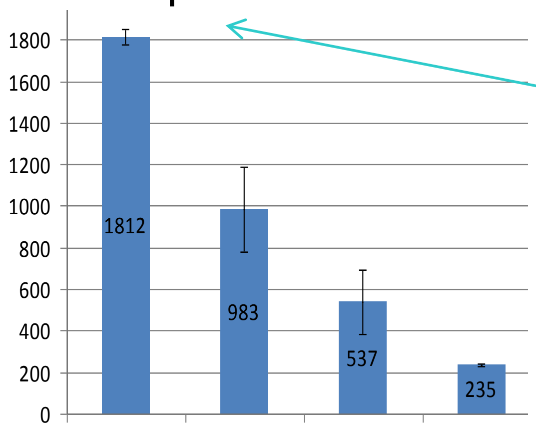
DSC



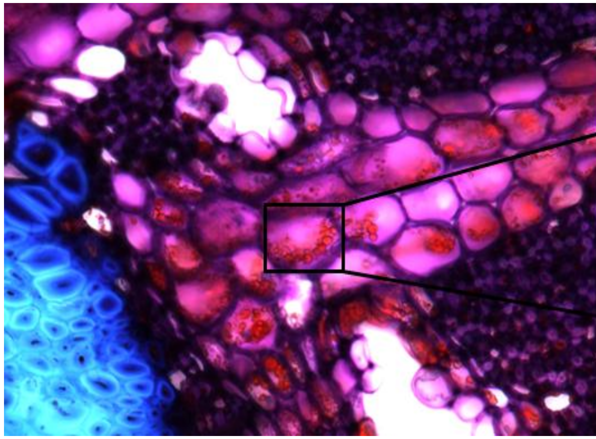


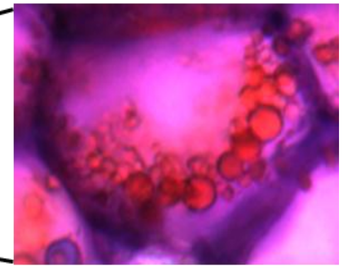
	CIRAD Latex	CIRAD Solvent/ bagasse	ISO 2000
Resin (%)	12 – 17	2-3	< 2
Mw (kg/mole)	2000-2200	1700-1800	2000 hevea
Ash (%)	0.2-1.2		< 1
Dirt (%)	0.02-0.05		<0.2
N total (%)	0.2-0.4		< 0.6

Mw vs process conditions



Imaging biomass during processing





PI extraction yield under latex form < 50% at pilot

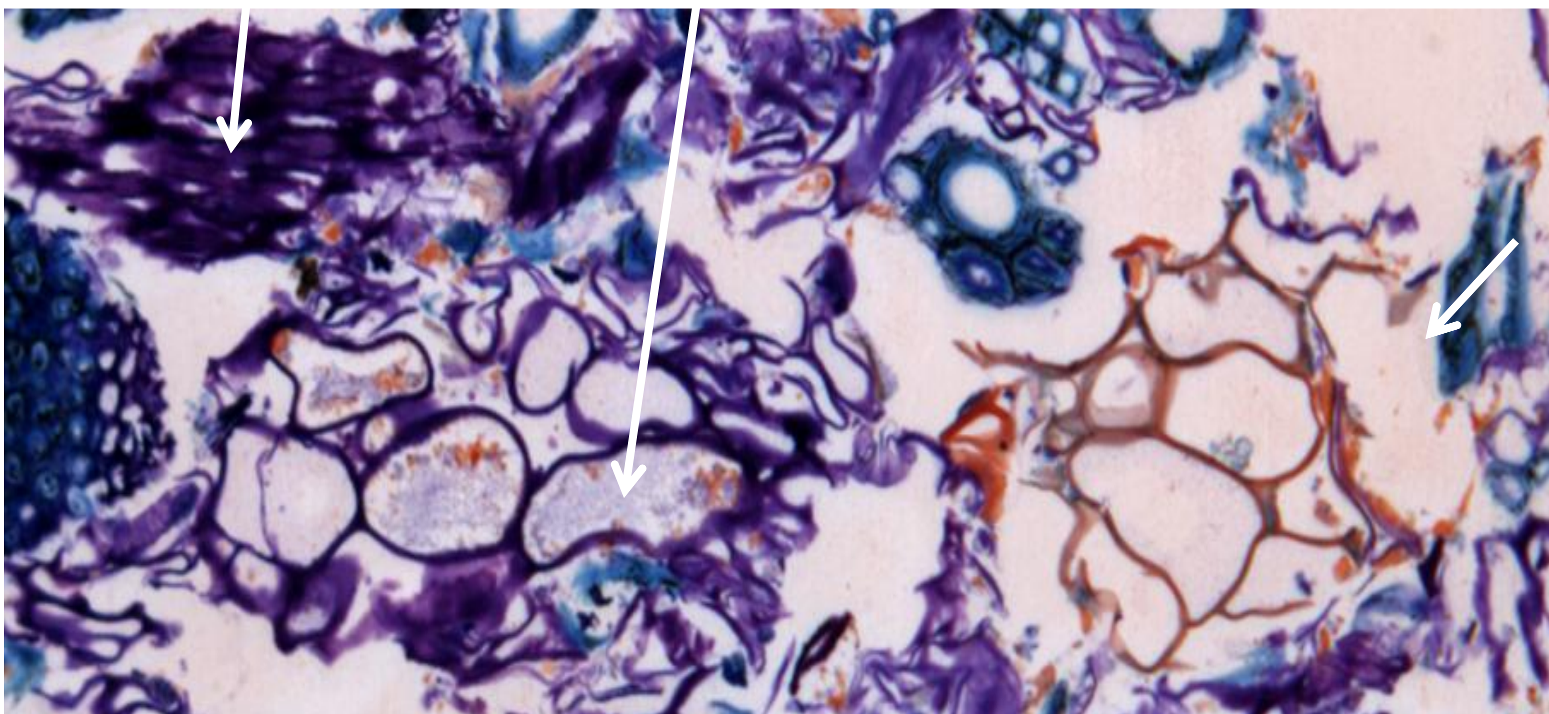
Starting biomass

PI particles
(red balls, points)

Cellular debris

Intact cell

Bagasse



Open cell

Sce: Cirad 2012
unpublished

Challenges & opportunities

Polyisoprene | Resin Terpen. Lipids | Proteins | Poly-sacchar. | Metals | Ligno cellulose

Cellular & molecular organization

Particle properties vs localization?

Chem. composition?

Role at interface?

Wall stability deconstruction

Physicochemistry / interface?

In-cell stability & PI loss?

Cropping

Harvest date / PI & resin %

Pretreatment ?

Storage ?

Processing options

Extract. PI by non solvent

Rubber by green solvent

Transport of polymer across network

Role of surfactants / cell explosion

Functional properties of products

Resin & protein: role of each class / rubber quality?

Which could / should be kept in PI? PI quality enhancing or reducing

Markets

Latex Rubber bioactive adhesion veg. oil biofuels ……

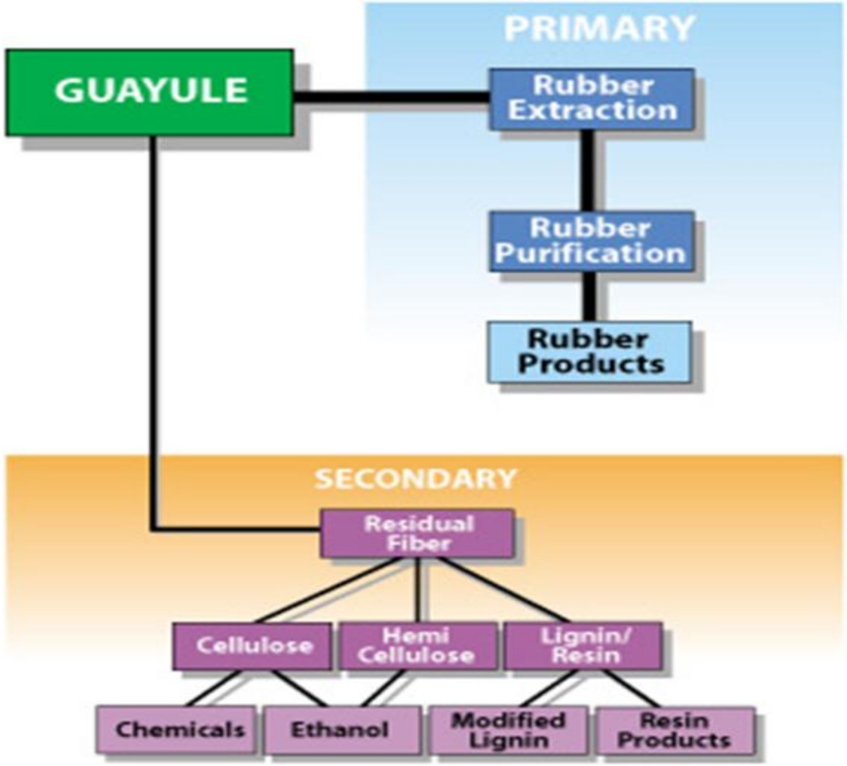
PROSPECT: Starting / Developing Guayule business

A few leaders worldwide, but currently developing their business

PanAridus and USDA-Bridgestone Am., seed producers

Yulex, biomass and commercial latex producer;
since 2011:
new production facility (latex & rubber);
links with manufacturers
Ansell (gloves) & Cooper (tires)
USDA grant 6.9 MD for R&D (biofuel)

Willing to apply the biorefinery concept



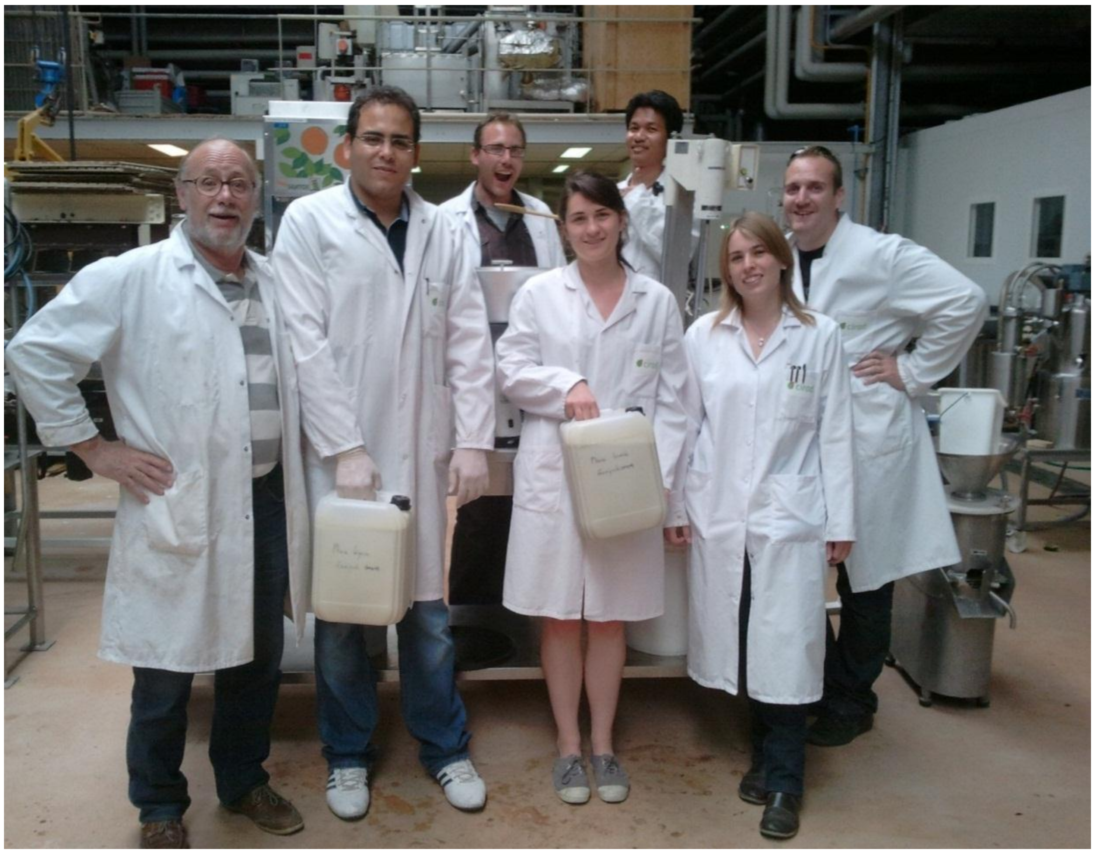
Overview of Guayule biomass processing
and delivered intermediate products at end of EU-Pearls
Prospect for next R&D steps

➡ **In less than 2 years; A working process** : 10-20 kg
for providing samples
scalable
→ **Gloves and tire** **“100% EU”** / biomass, process, rubber

➡ **Tuning resin & other extractible** to be separated
according to rubber quality & market for co-products

2 PhDs on the topic CIRAD + CTTM → higher latex yields

THANK YOU



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